

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 08-315819

(43)Date of publication of application : 29.11.1996

(51)Int.Cl.

H01M 4/58

H01M 4/02

H01M 10/40

(21)Application number : 07-123622

(71)Applicant : YUASA CORP

(22)Date of filing : 23.05.1995

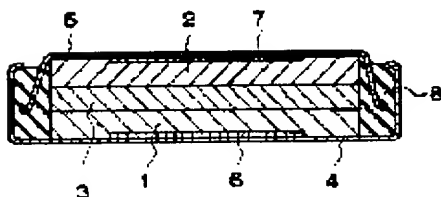
(72)Inventor : INAMASU TOKUO  
KURIYAMA KAZUYA

(54) SECONDARY BATTERY

(57)Abstract:

PURPOSE: To provide a lithium secondary battery with high energy density and excellent rate characteristics by replacing part of nickel atoms in a positive electrode active material with B, Al, In, and Sn, and adding Co, Mn, and Fe.

CONSTITUTION: A positive electrode active material of a lithium secondary battery is formed with a compound oxide having layer structure represented by  $\text{Li}_a\text{Ni}_b\text{M}_1\text{cM}_2\text{dM}_3\text{cO}_2$ . M1 is at least one element selected from Co, Mn, and Fe. M2 is at least one element selected from B, Al, In, and Sn. M3 is at least one element selected from Mg and Zn. A positive electrode 1 using this positive electrode active material is pressed against a positive can 4 through a positive electrode current collector 6. A lithium foil of a negative electrode is pressed against a negative can 5 through a negative electrode current collector 7. The positive electrode can 4 is fit to



the negative electrode can 5 through a separator 3 to assemble a coin type lithium battery.

## LEGAL STATUS

[Date of request for examination]

25.09.2001

[Date of sending the examiner's decision of rejection]

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[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3536947

[Date of registration]

26.03.2004

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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## CLAIMS

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[Claim(s)]

[Claim 1] Positive active material is  $\text{Li}_a\text{Ni}_b\text{M}_1\text{cM}_2\text{dM}_3\text{eO}_2$ . It consists of a multiple oxide which has the layer structure shown. M1 It is one or more sorts of elements chosen from Co, Mn, and Fe at least, and is M2. It is one or more sorts of elements chosen from B, aluminum, In, and Sn at least, and is M3. Rechargeable battery characterized by being one or more sorts of elements chosen from Mg and Zn at least.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the positive active material in more detail about a lithium secondary battery.

[0002]

[Description of the Prior Art] In recent years, the cell which uses a carbon material for a negative electrode for the active material which operating potential shows 4V order for the formation of a high energy consistency, or reinforcement attracts attention.  $\text{LiCoO}_2$  if the operating potential of a positive electrode is not high even if it is the case where a carbon material is used for a negative electrode for reinforcement, since it will say that a high energy consistency cell is hard to be obtained  $\text{LiNiO}_2$  etc. --  $\text{LiMO}_2$  The compound or  $\text{LiMn}_2\text{O}_4$  which has the layer structure shown etc. --  $\text{LiM}_2\text{O}_4$  The compound which has the Spinel structure shown is proposed and the part is already put in practical use.

[0003]

[Problem(s) to be Solved by the Invention] However,  $\text{LiCoO}_2$  A price's being high and capacity are small in resource and few, and cobalt is inadequate. Moreover,  $\text{LiNiO}_2$  using nickel stable in resource  $\text{LiCoO}_2$  That degradation of the capacity accompanying a cycle is large while it compares and capacity is large, and  $\text{LiCoO}_2$  It compared and there was a problem in putting in practical use according to the stable composition on a mass-production scale being difficult.

[0004] It is  $\text{LiNiO}_2$  in order to solve these problems. The researches and developments which permute and compound-ize some nickel are also done briskly. For example, at JP,62-264560,A, JP,63-114063,A, JP,63-211565,A, JP,63-299056,A, JP,1-120765,A, JP,2-40861,A, and JP,5-325966,A, it is  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ . It is  $\text{LiNiO}_2$  although using the multiple oxide shown for a positive electrode is proposed. It compares and initial capacity is falling.

[0005] Moreover, JP,62-256371,A, JP,5-101827,A, JP,5-198301,A, JP,5-283076,A, JP,5-299092,A, JP,6-96768,A, etc. are  $\text{LiNiO}_2$ . Although permuting some inner nickel with various transition metals, such as Co, V, Cr, Fe, Cu, Mg, Ti, and Mn, is proposed, an improvement of a cycle property is inadequate.

[0006] On the other hand, at JP,4-253162,A, it is  $\text{LiCoO}_2$ . Permuting a part of Co by Pb,

Bi, and B is proposed, and it is a general formula  $A_x M_y N_z O_2$  at JP,4-24831,B. Permuting by the transition-metals elements M, such as nickel, by at least one sort of elements N in aluminum, In, and Sn is proposed. Furthermore at JP,5-54889,A, it is a general formula  $Lix My Lz O_2$ . Permuting by one sort or two sorts or more of elements L chosen as the transition-metals elements M, such as nickel, from metallic elements, such as a nonmetallic element of the periodic tables IIIB and IVB and VB group and a semimetal element, an alkaline-earth-metal element, and Zn, Cu, Ti, is proposed.

[0007] However,  $LiCoO_2$  It is  $LiNiO_2$  to the permutation in Element L having been easy for in a part of Co then. It turned out that composition of the active material which permuted some nickel by Element L is difficult, and Element L is not incorporated in structure, but it remains as an impurity in an active material, and has a bad influence on cell engine performance, such as decline in charge-and-discharge effectiveness, and increase of self-discharge. although a reason cannot be concluded --  $LiNiO_2$  a case --  $LiCoO_2$  It compares and is hard to take the layer structure, and growth to C shaft orientations is made to check in a crystal growth phase, the permutation of Element L cannot take place easily, and Element L is considered to have remained as an impurity.

[0008] Furthermore,  $LiNiO_2$  The own resistance of an active material became high and the active material which permuted some nickel by Element L had a problem in the rate property, although the cycle property improved. It is  $LiNiO_2$  although a reason cannot be concluded. An ionic diffusion is controlled with a permutation element, the own resistance of an active material becomes high, and the active material which permuted some nickel by Element L is considered that the rate property fell.

[0009] This invention is made in view of the above-mentioned trouble, and the place made into the purpose is to offer the long lasting lithium secondary battery which was excellent in the rate property that an energy density is large.

[0010]

[Means for Solving the Problem] It is  $LiNiO_2$  as a result of examining the above-mentioned technical problem wholeheartedly. When it set and elements, such as B, aluminum, In, and Sn, permuted some nickel, by adding Co, Mn, and Fe showed becoming very easy. For Co, Mn, and Fe, this reason is same  $LiMO_2$  as nickel, although it cannot conclude. It is easy to take the layer structure of a mold, and it permutes, without checking growth to C shaft orientations by adding Co, Mn, and Fe. It is  $LiNiO_2$  by this. In inside, B, aluminum, In, Sn, etc. and both the elements of Co, Mn, and Fe can permute easily, and can take the layer structure. Therefore,  $LiNiO_2$  It is thought that inner nickel was able to be permuted by homogeneity, without having begun by adding elements, such as B, aluminum, In, and Sn, to Co, Mn, Fe, and coincidence, and checking growth to C shaft orientations.

[0011] Moreover,  $LiNiO_2$  The reason for having chosen permuting some inner nickel by elements, such as B, aluminum, In, and Sn, is shown below.

[0012] Although it is known that B, aluminum, and In will take trivalent and Sn will take tetravalence, such an element is not contributed to a cell reaction.

[0013] In the part permuted by the trivalent elements B, aluminum, and In, it exists in the form where the lithium was fixed. This part plays the role like a column of Li layer, suppresses repulsion between oxygen layers in the condition after charge, and controls change of the crystal structure. When furthermore inquired, these elements B, aluminum, and In existed in the crystal uniformly by existence of Co, Mn, and Fe, and it turned out

that the effectiveness is demonstrated. It distributes uniformly and the lithium which remains between oxygen layers as a result has also heightened the effectiveness.

[0014] Moreover, since it has combined with oxygen strongly, the part permuted by the tetravalent element Sn suppresses repulsion between oxygen layers in the condition after charge, and controls change of the crystal structure. When furthermore inquired, it turned out that Sn element exists in a crystal uniformly by existence of Co, Mn, and Fe, and the effectiveness is demonstrated. Consequently, on the whole, repulsion is controlled between oxygen layers, and the effectiveness is heightened.

[0015] Therefore, the active material of this invention is conventional  $\text{LiNiO}_2$  by the above effectiveness. By comparing, since deeper charge and discharge are possible, capacity increases and the capacity fall after cycle progress is considered to be a small thing.

[0016] Furthermore,  $\text{LiNiO}_2$  which performed the above permutations In permuting some nickel by Mg and Zn further, the own resistance of an active material decreases and it thinks as follows as a cause that the rate property has been improved. Although Li element which does not run by permuting by elements, such as B, aluminum, In, and Sn, under existence of Co, Mn, and Fe in the crystal structure contributes to the crystal stability at the time of charge, Li which does not participate in this charge and discharge is strongly connected with permutation elements, such as B, aluminum, In, and Sn, that lithium checks diffusion of the lithium of a under [ a crystal ], as a result, the own resistance of an active material increases, and a rate property is considered to have worsened. By adding Mg and Zn during such a crystal, connection of permutation elements, such as B, aluminum, In, and Sn, and a lithium is eased. Consequently, the lithium diffusion between layers is promoted, the own resistance of an active material decreases, and it is thought that the rate property has been improved.

[0017]

[Function]  $\text{LiNiO}_2$  The reason whose rate property whose increment and cycle property of capacity will improve under existence of Co, Mn, and Fe if elements, such as B, aluminum, In, and Sn, permute, and improves in permuting by Mg and Zn further is considered as follows.

[0018] Generally, it is  $\text{LiNiO}_2$ . If it charges with deep depth, change of the crystal structure will be caused and collapse of the crystal structure will be caused further. When Li in the layer structure falls out, repulsion between oxygen layers takes place, it changes to the more stable crystal structure, or bearing repulsion cannot be finished and a crystal collapses.

[0019] On the other hand,  $\text{LiNiO}_2$  Since the part by which Li does not move into the layer structure by permuting some inner nickel by element like B, aluminum, In, and Sn under existence of Co, Mn, and Fe can be made and the repulsive force between oxygen can be suppressed, change and collapse of the crystal structure can be prevented.

Therefore, conventional  $\text{LiNiO}_2$  He compares and it is thought that the cycle stability which was excellent even if it performed deep charge and discharge is shown.

[0020] Here, the lithium which does not participate in the charge and discharge connected with an element like B, aluminum, In, and Sn checks diffusion of a lithium in a crystal, as a result, the own resistance of an active material increases, and a rate property is considered to have worsened. By adding Mg and Zn during such a crystal, connection of permutation elements, such as B, aluminum, In, and Sn, and a lithium is eased.

Consequently, the lithium diffusion between layers is promoted, the own resistance of an active material decreases, and it is thought that the rate property has been improved.

[Example] Hereafter, the example of this invention is explained below.

[0021] (Example 1) if in charge of preparation of a lithium multiple oxide which has the layer structure, the mole ratio of Li:nickel:Co:B:Mg is set to 1.03:0.88:0.10:0.01:0.01 using LiOH-H<sub>2</sub>O, nickel<sub>2</sub>CO<sub>3</sub>, CoCO<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>, and MgO -- as -- weighing capacity -- it mixed and calcinated at 750 degrees C among oxygen for 20 hours. The object which cooled in after [ baking ] dry air and was ground in the desiccation ambient atmosphere was used as positive active material.

[0022] It turned out that the crystal is obtained more with the single phase in the X diffraction pattern of the obtained positive active material.

[0023] The coin mold lithium secondary battery was made as an experiment as follows using this active material. An active material, acetylene black, and polytetrafluoroethylene powder were mixed by the weight ratio 85:10:5, toluene was added, and it kneaded enough. This was fabricated with a thickness of 0.8mm in the shape of a sheet with the roller press. next, this -- the diameter of 16mm -- it pierced circularly, and heat-treated at 200 degrees C under reduced pressure for 15 hours, and the positive electrode 1 was obtained. The positive electrode 1 was stuck by pressure and used for the positive-electrode can 4 to which the positive-electrode charge collector 6 was attached. The negative electrode 2 pierced the lithium foil with a thickness of 0.3mm in a circle with a diameter of 15mm, and stuck by pressure and used it for the negative-electrode can 5 through the negative-electrode charge collector 7. It is LiPF<sub>6</sub> to the partially aromatic solvent of the volume ratio 1:1 of ethylene carbonate and diethyl carbonate. The fine porosity film made from polypropylene was used for the separator 3 using the electrolytic solution which carried out 1 mol/l dissolution. The with a diameter thickness [ 1.6mm thickness of 20mm ] coin mold lithium cell was produced using the above-mentioned positive electrode, a negative electrode, the electrolytic solution, and a separator. This cell is set to A1.

[0024] (Example 2) B<sub>2</sub>O<sub>3</sub> aluminum(NO<sub>3</sub>)<sub>3</sub> and 9H<sub>2</sub>O were used instead, and the cell was produced like the above-mentioned example 1 except carrying out weighing capacity so that the mole ratio of Li:nickel:Co:aluminum:Mg may be set to 1.03:0.88:0.10:0.01:0.01. The X diffraction pattern of the obtained positive active material showed that the crystal was obtained with the single phase. This cell is set to A2.

[0025] (Example 3) B<sub>2</sub>O<sub>3</sub> In(NO<sub>3</sub>)<sub>3</sub> and xH<sub>2</sub>O were used instead, and the cell was produced like the above-mentioned example 1 except carrying out weighing capacity so that the mole ratio of Li:nickel:Co:In:Mg may be set to 1.03:0.88:0.10:0.01:0.01. The X diffraction pattern of the obtained positive active material showed that the crystal was obtained with the single phase. Let this cell be A3.

[0026] (Example 4) B<sub>2</sub>O<sub>3</sub> SnO was used instead and the cell was produced like the above-mentioned example 1 except carrying out weighing capacity so that the mole ratio of Li:nickel:Co:Sn:Mg may be set to 1.03:0.88:0.10:0.01:0.01. The X diffraction pattern of the obtained positive active material showed that the crystal was obtained with the single phase. Let this cell be A4.

[0027] (Example 4) ZnO was used instead of MgO and the cell was produced like the above-mentioned example 1 except carrying out weighing capacity so that the mole ratio of Li:nickel:Co:B:Zn may be set to 1.03:0.88:0.10:0.01:0.01. The X diffraction pattern of

the obtained positive active material showed that the crystal was obtained with the single phase. Let this cell be A5.

[0028] (Example 1 of a comparison) LiOH-H<sub>2</sub>O and NiCO<sub>3</sub> Using, everything but carrying out weighing capacity so that the mole ratio of Li:nickel may be set to 1.03:1.00 produced the cell like the above-mentioned example 1. The X diffraction pattern of the obtained positive active material showed that the crystal was obtained with the single phase. This cell is set to B1.

[0029] (Example 2 of a comparison) LiOH-H<sub>2</sub>O, NiCO<sub>3</sub>, and CoCO<sub>3</sub> Using, everything but carrying out weighing capacity so that the mole ratio of Li:nickel:Co may be set to 1.03:0.90:0.10 produced the cell like the above-mentioned example 1. The X diffraction pattern of the obtained positive active material showed that the crystal was obtained with the single phase. Let this cell be B-2.

[0030] (Example 3 of a comparison) LiOH-H<sub>2</sub>O, NiCO<sub>3</sub>, and B-2 O<sub>3</sub> Using, everything but carrying out weighing capacity so that the mole ratio of Li:nickel:B may be set to 1.03:0.90:0.10 produced the cell like the above-mentioned example 1. The X diffraction pattern of the obtained positive active material to LiNiO<sub>2</sub> Lamellar crystal growth was bad and it was checked that it is the mixture of the compound which cannot fully be specified. Furthermore, when the chemical analysis of the obtained positive active material is performed, divalent nickel remains and it is guessed that sufficient oxidation of nickel did not take place. This cell is set to B3.

[0031] (Example 4 of a comparison) LiOH-H<sub>2</sub>O, NiCO<sub>3</sub>, CoCO<sub>3</sub>, and B-2 O<sub>3</sub> Using, everything but carrying out weighing capacity so that the mole ratio of Li:nickel:CoB may be set to 1.03:0.89:0.10:0.01 produced the cell like the above-mentioned example 1. The X diffraction pattern of the obtained positive active material showed that the crystal was obtained with the single phase. Let this cell be B4.

[0032] Thus, the charge-and-discharge cycle trial was performed using the produced cells A1 and A2, A3, A4, A5, B1, B-2, B3, and B4. The test condition was set to 3mA of charging currents, charge termination electrical-potential-difference 4.2V, 3mA of discharge currents, 10mA, and discharge-final-voltage 3.0V.

[0033] The result of the charge and discharge test of the these-produced cell is shown in Table 1.

[0034]

[Table 1]

電池	放電電流 3mA 放電容量(mAh)		放電電流 10mA 放電容量(mAh)	
	1サイクル	10サイクル	1サイクル	10サイクル
A1	65	64	58	55
A2	66	63	57	54
A3	65	64	57	55
A4	66	64	56	53
A5	66	63	55	52
B1	52	45	28	25
B2	50	43	29	24
B3	49	40	30	25
B4	63	62	30	28

[0035] As shown in Table 1, the cells A1 and A2 by this invention, A3, A4, and A5 had a large initial charge-and-discharge capacity compared with the comparison cell B1, B-2, and B3, and its reduction of the capacity after 10 cycles was small. Furthermore,

compared with comparison cell B4, as for the cells A1 and A2 by this invention, A3, A4, and A5, it turned out that the rate property is improved.

[0036] Thus,  $\text{LiNiO}_2$  An improvement of a rate property and the stability of a cycle will not be realizable without permuting nickel under Co, Mn, Fe, and coexistence of B, aluminum, In, and Sn, and permuting by Mg or Zn further.

[0037] In addition, this invention is not limited to the start raw material, the manufacture approach, a positive electrode, a negative electrode, an electrolyte, a separator, a cell configuration, etc. of the active material indicated by the above-mentioned example. Moreover, it is applicable to what uses a carbon material for a negative electrode, an electrolyte, the thing which uses a solid electrolyte instead of a separator, etc.

[0038]

[Effect of the Invention] Since this invention is constituted like \*\*\*\*, the long lasting lithium secondary battery excellent in reversibility with a large discharge capacity can be offered.

